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between about 0.910 and 0.935 grams per cubic centimeter (g/cc).

Ethylene polymers and copolymers prepared by the use of a coordination catalyst, such as a Ziegler or Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone. High density polyethylene (HDPE), generally having a density of about 0.941 to about 0.965 g/cc, is typically a homopolymer of ethylene, and it contains relatively few branch chains relative to the various linear copolymers of ethylene and an  $\alpha$ -olefin. HDPE is well known, commercially available in various grades, and is useful in this invention.

Linear copolymers of ethylene and at least one  $\alpha$ -olefin of 3 to 12 carbon atoms, preferably of 4 to 8 carbon atoms, are also well known, commercially available and useful in this invention. As is well known in the art, the density of a linear ethylene/ $\alpha$ -olefin copolymer is a function of both the length of the  $\alpha$ -olefin and the amount of such monomer in the copolymer relative to the amount of ethylene, the greater the length of the  $\alpha$ -olefin and the greater the amount of  $\alpha$ -olefin present, the lower the density of the copolymer. Linear low density polyethylene (LLDPE) is typically a copolymer of ethylene and an  $\alpha$ -olefin of 3 to 12 carbon atoms, preferably 4 to 8 carbon atoms (e.g., 1-butene, 1-octene, etc.), that has sufficient  $\alpha$ -olefin content to reduce the density of the copolymer to that of LDPE. When the copolymer contains even more  $\alpha$ -olefin, the density will drop below about 0.91 g/cc and these copolymers are known as ultra low density polyethylene (ULDPE) or very low density polyethylene (VLDPE). The densities of these linear polymers generally range from about 0.87 to 0.91 g/cc.

Both the materials made by the free radical catalysts and by the coordination catalysts are well known in the art, as are their methods of preparation. Relevant discussions of both of these classes of materials, and their methods of preparation, are found in U.S. Pat. No. 4,950,541 and the patents to which it refers, all of which are incorporated herein by reference.

The homogeneously branched polyethylenes that can be used in the practice of this invention also fall into two broad categories, the linear homogeneously branched and the substantially linear homogeneously branched. Both are known. The former and their method of preparation are described in U.S. Pat. No. 3,645,992 to Elston, and the latter and their method of preparation are fully described in U.S. Pat. Nos. 5,272,236 and 5,278,272, all of which are incorporated into and made a part of this application by reference. Examples of the former are the Tafmer<sup>TM</sup> polymer of Mitsui and the Exact<sup>TM</sup> polymer of Exxon, while an example of the latter are the polymers made by the Insite<sup>TM</sup> Technology of The Dow Chemical Company.

As here used, "substantially linear" means that the polymer backbone is substituted with about 0.01 long-chain branches/1000 carbons to about 3 long-chain branches/1000 carbons, preferably from about 0.01 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons, and more preferably from about 0.05 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons. In contrast, simply "linear" means that long chain branching is essentially absent from the polymer backbone. Long-chain branching is here defined as a chain length of at least about 6 carbon atoms, above which the length cannot be distin-

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guished using  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy, yet the long-chain branch can be about the same length as the length of the polymer backbone.

These unique substantially linear homogeneously branched polymers (subsequently referred to as "substantially linear ethylene polymers") are prepared by using constrained geometry catalysts (CGC), and are characterized by a narrow molecular weight distribution and if an interpolymer, by a narrow comonomer distribution. As here used, "interpolymer" means a polymer of two or more comonomers, e.g. a copolymer, terpolymer, etc. Other basic characteristics of these substantially linear ethylene polymers include a low residuals content (i.e. low concentrations in the substantially linear ethylene polymer of the catalyst used to prepare the polymer, unreacted comonomers, if any, and low molecular weight oligomers made during the course of the polymerization), and a controlled molecular architecture which provides good processability even though the molecular weight distribution is narrow relative to conventional olefin polymers.

While the substantially linear ethylene polymers used in the practice of this invention include substantially linear ethylene homopolymers, preferably these substantially linear ethylene polymers comprise between about 95 and 50 wt % ethylene, and about 5 and 50 wt % of at least one  $\alpha$ -olefin comonomer, more preferably 10 to 25 wt % of at least one  $\alpha$ -olefin comonomer. Percent comonomer is measured by Infrared Spectroscopy according to ASTM D-2238 Method B. Typically, the substantially linear ethylene polymers are copolymers of ethylene and an  $\alpha$ -olefin of 3 to about 20 carbon atoms (e.g. propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, styrene, etc.), with a density of 0.850 to about 0.960 grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ), preferably of 0.870 to about 0.910  $\text{g}/\text{cm}^3$ . The melt flow ratio, measured as  $I_{10}/I_2$  (ASTM D-1238), is greater than or equal to 5.63, and is preferably from about 6.5 to 15, more preferably from about 7 to 10. The molecular weight distribution ( $M_w/M_n$ ), measured by gel permeation chromatography (GPC), is defined by the equation:

$$M_w M_n \leq (I_{10}/I_2) - 4.63,$$

and is preferably between about 1.5 and 2.5. For the substantially linear ethylene polymers, the  $I_{10}/I_2$  ratio indicates the degree of long-chain branching, i.e. the larger the  $I_{10}/I_2$  ratio, the more long-chain branching in the polymer.

The "theological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R. N. Shiroff and L. V. Cancio in *Polymer Engineering Science*, Vol. 17, No. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99, both publications of which are incorporated herein by reference. GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 250 to 5500 psig using about a 7.54 cm diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of  $2.15 \times 10^6$  dyne/CM<sup>2</sup>. These substantially linear ethylene interpolymers and homopolymers preferably have a PI in the range of about 0.01 kpoise to about 50

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## POLYOLEFIN BLENDS AND THEIR SOLID STATE PROCESSING

### BACKGROUND OF THE INVENTION

This invention relates to polyolefin blends. In one aspect, the invention relates to polyolefin blends suitable for solid state processing while in another aspect, the invention relates to particular blends of various polyethylenes. In still another aspect, the invention relates to polyolefin blends characterized by melting and crystallization curves exhibiting either two distinct melt regions, or wherein one component has a softening point lower than that of a conventional polyolefin, either technique of which provides an unusually wide window for solid state processing.

While the field of metal forming offers a wide variety of solid state processing, e.g. stamping, forging, rolling, extrusion, etc., the solid state processing of semicrystalline polymers is much more limited. To process a thermoplastic in the solid state, typically the processing temperature is maintained at just a few degrees below the melting point of the polymer. If the processing temperature is above the melting point of the polymer, then the processing is simply a melt extrusion. At temperatures considerably below the melting point of the polymer, the polymer is essentially a solid and its deformation requires a tremendous amount of pressure (often in excess of one million psi). Such enormous pressures make large deformations very difficult, and result in a relatively low production rate and a generally energy inefficient process. Moreover, since the processing temperature is the most critical parameter in solid state processing, this technique has been limited to those polymers and polymer blends with relatively wide (e.g. at least about 20 degrees on the Celsius scale) ranges between their softening and melting temperatures. Since this temperature range is relatively narrow for conventional polyolefins and their blends, these materials have not been the subject of extensive, commercial-scale solid state processing.

Despite their relatively narrow processing temperature window, the sheer commercial scale of the polyolefin market has generated considerable interest in applying this technique to polyolefins. The potential benefits to be gained include energy efficiency, speed, and scrap reduction. Ciferri and Ward in "Ultra High Modulus Polymers", *Applied Science Publications*, London (1979), teach that the extrusion of polymers below the melting point is a promising method of producing highly oriented materials. Kryuchkov, et al. in *Polymer Composite*, Vol. 7, No. 6, pp. 413-420 (1986), disclosed the detailed investigations of the dynamics of solid state extrusion, and they have also postulated a model to correlate the flow of instability in extrudate defects to the extrusion temperature and pressure.

Chung in U.S. Pat. No. 5,028,663 teaches that certain blends of high density polyethylene (HDPE) and low density polyethylene (LDPE) prepared by solution mixing can achieve a broader operating window for certain solid state processing applications than would otherwise be achieved by mechanical mixing. The melting peak of each component in the blend is separated due to solution precipitation such that large deformation processing can be performed at a temperature between the melting peaks of the two components.

Pawlowski, et al. in U.S. Pat. Nos. 4,352,766, 4,161,502 and 3,739,052 teach a unique process called Solid Phase

Forming (SPF) to form polymers and composites at a pre-melt state. This unique fabrication process induces a biaxial orientation throughout the finished parts.

Enikolopow, et al. in U.S. Pat. No. 4,607,797 teach a process called Solid State Shear Extrusion or Pulverization to perform polymer extrusion at a temperature below the peak melting temperature of the polymer. However, Shutov has observed in a 1992 J.I.T. Research Report that certain polymers, such as HDPE, polypropylene (PP) and polycarbonate (PC) did not perform well in this process.

The disclosures of each of the patents referenced above are incorporated herein by reference.

### SUMMARY OF THE INVENTION

According to this invention, polyolefin blends characterized by melting and crystallization curves which exhibit either two distinct melt regions, or a low softening point relative to the high melting component of the blend, provide an unusually wide window for solid state processing. These blends comprise at least 10 percent by weight of the low melting component, and the difference between the peak melting temperature of the low melting component and the high melting component is at least about twenty degrees on the Celsius scale. These blends are processed in their solid state at a temperature above about the peak melting temperature of the low melting component and below the peak melting temperature of the high melting component. The solid state processing characteristics of the blends of this invention are independent of the manner in which the components are mixed, e.g. mechanical, solvent, etc.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polyolefin blends of this invention comprise two or more, typically two, polyolefin components. These blends are characterized by having a solid state processing temperature ( $T_p$ ) defined by

$$T_{m2} < T_p < T_{m1}$$

in which the  $T_{m2}$  is the peak melting temperature of the high melting component, and  $T_{m1}$  is the peak melting temperature of the low melting component. Typically, the difference or range between  $T_{m2}$  and  $T_{m1}$ , i.e.  $T_{m2} - T_{m1}$ , is greater than about twenty, preferably greater than about thirty, and most preferably greater than about forty, degrees on the Celsius scale.

The components of the blends of this invention are polyolefins, e.g. polyethylenes, polypropylenes, dienes, styrene, etc. Preferred polyolefins are the various polyethylenes and polypropylenes, and preferred blends are those containing at least one polyethylene, particularly a substantially linear ethylene polymer.

The polyethylenes can be divided into two broad classes, heterogeneously branched and homogeneously branched. The heterogeneously branched polyethylenes that can be used in the practice of this invention fall into two broad categories, those prepared with a free radical initiator at high temperature and high pressure, and those prepared with a coordination catalyst at high temperature and relatively low pressure. The former are generally known as low density polyethylenes (LDPE) and are characterized by branched chains of polymerized monomer units pendant from the polymer backbone. LDPE polymers generally have a density

has included laboratory management including supervision of microscopy, thermal analysis, and spectroscopy. Since 1991 my focus has been in product development in the polymer science group of Research Development, and Engineering.

3. Prior to April 26, 1993 I made a heat-shrinkable film for use in a heat-shrinkable patch bag structure, and prior to April 26, 1993, I also tested this film and determined that it had an impact strength high enough to be used as a heat-shrinkable patch film in a heat-shrinkable patch bag, as evidenced by the following:

- 3a. Prior to April 26, 1993, I prepared and tested a Control Film (Exhibit A) as well as a First Experimental Film (Exhibits B1 and B2) and a Second Experimental Film (Exhibits C1 and C2);
- 3b. The Control Film was designated as "B003" (See Exhibit A), which is the Cryovac manufacturing code for the commercialized film to be used as a patch film for a patch bag; the Control film had a thickness of 4.5 mils, and had an A/B//B/A structure in which A represented a blend of 87% LLDPE, 10% EVA, and 3% additive package, and B represented 100% EVA (all resin codes have been redacted from each of Exhibits A, B1, B2, C1, and C2, with the code names being replaced in red ink with generic names substituted therefor, to aid in understanding the exhibits);
- 3c. The First Experimental Film had the same thickness and layer arrangement as the Control Film (see Exhibit B1), and was designated "FDX 4315" (see Exhibit B2), while Exhibit B1 is a notebook page providing the manufacturing details associated with the developmental production run, Exhibit B2 is a page from the developmental film structures notebook which provides the layer arrangement and composition for this same film, the notebook pages of Exhibits B1 and B2 correspond with one another, as can be seen from the fact that the multilayer structure of Exhibit B1 corresponds with the multilayer

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5/17/01~~DO NOT ENTER~~ ~~TO ENTER~~ ~~PATCH~~ BAG COMPRISING HOMOGENEOUS ETHYLENE/ALPHA-OLEFIN COPOLYMER~~DO AS ENTERED~~

## 1. Field of the Invention

5 The present invention relates to packages for the packaging of bone-in meat products. More particularly, the present invention relates to a bag having a protective patch adhered directly thereto, the protective patch preventing, or reducing, puncture of the bag by exposed bone from a meat product within the bag.

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## 2. Background of the Invention

15 Heat-shrinkable thermoplastics are known to be useful as flexible packaging materials for vacuum packaging various foodstuffs, including meat. Such plastic materials, however, while generally suitable for packaging meat, understandably have difficulties in successfully packaging sharp or bony products. For example, attempts to package bone-in primal cuts of meat usually result in an unsatisfactorily large number of bag failures due to exposed bone puncturing the bag.

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25 The use of cushioning materials such as paper, paper laminates, wax impregnated cloth, and various types of plastic inserts have proved to be less than totally satisfactory in solving the problem, as they require large expenditure of materials and labor, and are subject to shifting off of protruding bones. The preparation of special cuts of meat or close bone trim with removal of protruding bones has also been attempted. However, this is at best only a limited solution to the problem since it does not offer the positive protection necessary for a wide variety of commercial bone-in types of meat. Furthermore, removal of the bone is a relatively expensive and time-consuming procedure.

30 Some time ago, the use of a bag having a patch thereon, i.e., a "patch bag", became a commercially-preferred manner of packaging a number of bone-in meat products. One of the first commercially-

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utilized patch bags utilized a heat shrinkable bag and a patch composed of two laminated VALERON (TM) high density polyethylene ("HDPE") films, each film having been highly oriented in the machine direction. In the laminated patch, the machine direction of a first HDPE lamina was oriented about 90 degrees with respect to the machine direction of a second patch lamina.

The VALERON (TM) HDPE patch performed well in preventing punctures from exposed bone. However, upon packaging a meat product in a heat-shrinkable bag having such a patch thereon, the corners of the patch delaminated from the bag upon shrinkage of the bag, due to the fact that the patch would not shrink as the bag shrank. Customers perceived the delamination of the patch corners from the bag to be highly undesirable. Furthermore, the highly oriented HDPE films were opaque white due to the formation of voids during the orientation process.

Thus, the need arose for a patch which would provide the patch bag with a desired level of puncture-resistance, while at the same time being heat-shrinkable so that there would be no substantial delamination at the corners of the patch. Furthermore, although for some uses it was desirable to use an opaque patch, for other uses it was desirable to provide a substantially translucent or transparent patch.

Although ethylene/vinyl acetate copolymer ("EVA") was known to have the desired heat shrink properties for use in patches, it was discovered to lack the desired level of puncture-resistance obtainable using the VALERON (TM) HDPE patch. That is, EVA patches had to be much thicker than an HDPE patch in order to provide the same level of puncture-resistance. Furthermore, in addition to lacking the desired puncture-resistant character, EVA lacked abrasion-resistance, further diminishing its utility as the bulk polymer in the patch.

Surprisingly, linear low density polyethylene (LLDPE) was found to provide the combination of puncture-resistance, heat-

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shrinkability, abrasion-resistance, and even transparency, desired for use in a patch for patch bags. Within the last 10 years, patch bags having patches composed of LLDPE have come into widespread commercial use in the United States.

5 However, LLDPE has several drawbacks. For example, LLDPE is not easily processable as it causes high extruder back pressure if extrusion is attempted at relatively high speeds. Furthermore, because of its stiffness, LLDPE is difficult to orient, which necessitates that another polymer be blended with the LLDPE in order to permit the desired orientation of the LLDPE to provide a shrinkable patch. Furthermore, LLDPE will not heat-seal to itself, necessitating the use of another type of polymer if the patch is to be formed from a collapsed film tube, as is one of the most desirable processes for manufacturing patches.

10 15 Thus, it would be desirable to locate another polymer which can provide the combination of puncture-resistance and heat-shrinkability. Furthermore, it would be desirable that this other polymer also be capable of being manufactured as a substantially transparent film. Furthermore, it would be desirable if this other polymer was easier to extrude than LLDPE, had a stiffness low enough to avoid the need to blend a stiffness-reducing polymer therewith, and had the ability to be heat-sealed to itself.

#### SUMMARY OF THE INVENTION

20 25 The present invention is directed to the use of homogeneous ethylene/alpha-olefin copolymer in a patch for a patch bag. This homogeneous polymer has surprisingly been found to provide a combination of puncture-resistance and heat-shrinkability which is at least the equivalent of LLDPE. Furthermore, it has also surprisingly been found that this homogeneous polymer has about the same abrasion-resistance as LLDPE, and can be used to form a substantially transparent heat shrinkable patch. Thus, this homogeneous polymer has been discovered to provide an alternative 30 to the use of LLDPE in patches for patch bags. At least some

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species of this homogeneous polymer are considerably easier to extrude than LLDPE. Furthermore, some species have a stiffness low enough to avoid the need to blend a stiffness reducing polymer therewith. Finally, at least some species of the polymer, when extruded into a tubular film, offer the further advantage of substantially better sealing to itself, relative to LLDPE.

As a first aspect, the present invention is directed to a patch bag comprising a heat-shrinkable patch adhered to a heat-shrinkable bag. The heat-shrinkable patch comprises a first heat-shrinkable film and the heat-shrinkable bag comprises a second heat-shrinkable film. The first heat-shrinkable film comprises a homogeneous ethylene/alpha-olefin copolymer.

Preferably, the patch bag further comprises an adhesive layer between the first heat-shrinkable film and the second heat-shrinkable film. Preferably, the homogeneous ethylene/alpha-olefin copolymer has a density of from about 0.87 to 0.94 g/cc, more preferably, 0.89 to 0.92. Preferably, the first heat-shrinkable film has a free shrink at 185°F of from about 10 to 100 percent, more preferably 15 to 75 percent, and still more preferably, 20 to 60 percent. Preferably, the first heat-shrinkable film has a free shrink, at 185°F, of from about 40 to 120 percent of the free shrink of the second heat-shrinkable film; more preferably, from 40 to 100 percent.

Preferably, the homogeneous ethylene/alpha-olefin is present in the first heat-shrinkable film in an amount of from about 5 to 100 weight percent, based on the weight of the first heat-shrinkable film; more preferably, from about 15 to 85 weight percent.

The first heat-shrinkable film can comprise a first homogeneous ethylene/alpha-olefin copolymer while the second heat-shrinkable film comprises a second homogeneous ethylene/alpha-olefin copolymer. The first and second homogeneous ethylene/alpha-olefin copolymers can be the same or different.

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Preferably, the first heat-shrinkable film comprises two outer layers and two inner layers, the two outer layers being substantially identical in chemical composition and thickness, and the two inner layers being substantially identical in chemical composition and thickness. In one preferred embodiment, each of the two outer layers comprises the homogeneous ethylene/alpha-olefin in an amount of from about 1 to 100 weight percent, based on the weight of the outer layers. Furthermore, each of the two inner layers comprises the homogeneous ethylene/alpha-olefin in an amount of from about 1 to 100 weight percent, based on the weight of the inner layers. In an alternative embodiment, each of the two outer layers is composed of a composition substantially free of homogeneous ethylene/alpha-olefin copolymer, with the two inner layers comprising homogeneous ethylene/alpha-olefin copolymer. Preferably, the two substantially identical inner layers each comprise at least one member selected from the group consisting of ethylene/vinyl ester copolymer, ethylene/vinyl acid copolymer, ionomer, and homogeneous ethylene/alpha-olefin copolymer having a density of from about 0.87 to 0.91 g/cc. Preferably, the ethylene/vinyl ester copolymer comprises at least one member selected from the group consisting of ethylene/methyl acrylate copolymer, and ethylene/vinyl acetate copolymer, and the ethylene/vinyl acid copolymer comprises ethylene/methacrylic acid copolymer. Preferably, the two substantially identical outer layers comprise from about 10 to 80 weight percent of the weight of the first heat-shrinkable film.

As a second aspect, the present invention pertains to a packaged product, comprising a package and a meat product in the package. The package includes a patch bag comprising a heat-shrinkable patch adhered to a heat-shrinkable bag, the heat-shrinkable patch comprising a first heat-shrinkable film and the heat-shrinkable bag comprising a second heat-shrinkable film, the first heat-shrinkable film comprising a homogeneous ethylene/alpha-

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olefin copolymer. The meat product comprises bone. Preferably, the meat product comprises at least one member selected from the group consisting of ham, spareribs, picnic, back rib, short loin, short rib, whole turkey, pork loin.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a schematic view of a preferred end-seal patch bag according to the present invention, in a lay-flat view.

10 Figure 2 illustrates a cross-sectional view of the end-seal patch bag illustrated in Figure 1, taken through section 2-2 of Figure 1.

15 Figure 3A illustrates a cross-sectional view of a preferred multilayer film suitable for use as the patch in the patch-bag according to Figure 1.

Figure 3B illustrates an enlarged cross-sectional view of the 20 multilayer film of Figure 3A.

Figure 3C illustrates a schematic cross-sectional view of a multilayer film described in Patch Film No. 19.

Figure 4 illustrates a schematic view of a preferred process for making the multilayer film of Figure 3.

25 Figure 5 illustrates a cross-sectional view of a preferred multilayer film suitable for use as the bag in the patch-bag according to Figure 1.

Figure 6 illustrates a schematic view of a preferred process for making the multilayer film of Figure 5.

20 Figure 7 illustrates a schematic view of a preferred process for making the patch bag of Figure 1, using the films of Figures 3 and 5, as respectively produced by the processes of Figures 4 and 6.

30 Figure 8 illustrates a perspective view of a shrunken patch bag containing a pair of fresh, bone-in whole pork loins, each viewed from the ham end.

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Figure 9 illustrates a cross-sectional view taken through section 9-9 of Figure 8, with the addition of a patch bag within which the pair of bone-in pork loins are packaged.

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#### DETAILED DESCRIPTION OF THE INVENTION

A film seal layer, i.e., sealing layer or heat seal layer, is an outer film layer, or layers, involved in the sealing of the film to itself, another film layer of the same or another film, and/or another article which is not a film. In general, up to the outer 10 3 mils of a film can be involved in the sealing of the film to itself or another layer. With respect to packages having only fin-type seals, as opposed to lap-type seals, the sealant layer includes the inside film layer of a package, as well as supporting layers adjacent this sealant layer, the inside layer frequently 15 also serving as a food contact layer in the packaging of foods.

In general, a sealant layer to be sealed by heat-sealing can comprise any thermoplastic polymer; preferably, the heat-sealing layer comprises, for example, thermoplastic polyolefin, thermoplastic polyamide, thermoplastic polyester, and thermoplastic 20 polyvinyl chloride; more preferably, thermoplastic polyolefin; still more preferably, thermoplastic polyolefin having less than 60 weight percent crystallinity. Preferred sealant compositions are the same as the compositions for the abuse layer, as set forth below.

25 A bag seal is a seal of a first region of a film surface to a second region of a film surface, wherein the seal is formed by heating the regions to at least their respective seal initiation temperatures. The heating can be performed by any one or more of a wide variety of manners, such as using a heated bar, hot air, 30 infrared radiation, ultrasonic sealing, etc.

A film barrier layer is a layer which serves as a barrier to one or more gases. Oxygen (i.e., O<sub>2</sub>) barrier layers can comprise, for example, ethylene/vinyl alcohol copolymer, polyvinyl chloride,

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polyvinylidene chloride, polyamide, polyester, polyacrylonitrile, etc., as known to those of skill in the art; preferably, the oxygen barrier layer comprises ethylene/vinyl alcohol copolymer, polyvinylidene chloride, and polyamide; more preferably, vinylidene chloride/methyl acrylate copolymer, as known to those of skill in the art.

As used herein, "EVOH" refers to ethylene/vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene/vinyl acetate copolymers, and refers to a vinyl alcohol copolymer having an ethylene comonomer, and prepared by, for example, hydrolysis of vinyl acetate copolymers, or by chemical reactions with polyvinyl alcohol. The degree of hydrolysis is preferably at least 50% and more preferably at least 85%.

A film abuse layer is a film layer which serves to resist abrasion, puncture, and other potential causes of reduction of package integrity, as well as potential causes of reduction of package appearance quality. Abuse layers can comprise any polymer, so long as the polymer contributes to achieving an integrity goal and/or an appearance goal; preferably, the abuse layer comprises polymer comprising at least one member selected from the group consisting of ethylene/alpha-olefin copolymer having a density of from about 0.85 to 0.95, propylene/ethylene copolymer, polyamide, ethylene/vinyl acetate copolymer, ethylene/methyl acrylate copolymer, and ethylene/butyl acrylate copolymer, etc. as known to those of skill in the art; more preferably, in the patch bag of the present invention the abuse layer of the patch comprises homogeneous ethylene/alpha olefin copolymer.

A film core layer is an inner film layer, i.e., internal film layer, which has a primary function other than serving as an adhesive or compatibilizer for adhering two layers to one another. Usually, the core layer, or layers, provides the multilayer film with a desired level of strength, i.e., modulus, and/or optics, and/or added abuse resistance, and/or specific impermeability.

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A film skin layer is an outside film layer, in a multilayer film used in the packaging of a product. The skin layer is subject to abuse. Accordingly, the preferred polymers for the skin layer are the same as the preferred polymers for the abuse layer.

5 A film tie layer is an inner layer of a multilayer film, this inner layer having the primary purpose of adhering two layers of the film to one another. Tie layers generally comprise any polymer having a polar group grafted thereon, so that the polymer is capable of covalent bonding to polar polymers such as polyamide and ethylene/vinyl alcohol copolymer; preferably, tie layers comprise at least one member selected from the group consisting of 10 polyolefin, modified polyolefin, ethylene/vinyl acetate copolymer, modified ethylene/vinyl acetate copolymer, and homogeneous ethylene/alpha-olefin copolymer; more preferably, tie layers comprise at least one member selected from the group consisting of 15 anhydride modified grafted linear low density polyethylene, anhydride grafted low density polyethylene, homogeneous ethylene/alpha-olefin copolymer, and anhydride grafted ethylene/vinyl acetate copolymer.

20 A film laminate is a film made by bonding together two or more layers of film or other materials. Lamination can be accomplished by joining layers with adhesives, joining with heat and pressure, and even spread coating and extrusion coating. Film laminates also include coextruded multilayer films comprising one or more tie 25 layers.

30 A heat-shrinkable film is typically made by first being stretched at an elevated temperature (the orientation temperature) which is below the melt temperature of at least one polymer present in the film. During the orientation process, the film is generally biaxially oriented by being "stretched" in the transverse direction, and "drawn" in the machine direction. Preferably, the application of substantial cooling occurs at some point downstream of the upstream roller, the point of cooling being dependent upon

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material properties and cooling rates. Ultimately, this type of process results in a film which is heat-shrinkable in both the transverse and longitudinal directions. Upon subsequently heating unrestrained, unannealed, oriented polymer-containing material to its orientation temperature, heat shrinkage is produced almost to the original unstretched, i.e., pre-oriented dimensions. The orientation in oriented films can be produced in one or more of a variety of manners.

The orientation ratio of a film is the multiplication product of the extent to which the plastic film material is expanded in several directions, usually two directions perpendicular to one another. "Drawing" is orientation in the machine direction, while "stretching" is orientation in the transverse direction. For films extruded through an annular die, stretching is obtained by "blowing" the film to produce a bubble. Drawing is obtained by passing the film through two sets of powered nip rolls, with the downstream set having a higher surface speed than the upstream set, with the resulting draw ratio being the surface speed of the downstream set of nip rolls divided by the surface speed of the upstream set of nip rolls. The degree of orientation is also referred to as the orientation ratio, or sometimes as the "racking ratio".

As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homopolymers, copolymers, terpolymers, etc. In general, the layers of a film can consist essentially of a single polymer, or can have still additional polymers together therewith, i.e., blended therewith.

As used herein, the term "copolymer" refers to polymers formed by the polymerization reaction of at least two different monomers. For example, the term "copolymer" includes the copolymerization reaction product of ethylene and an alpha-olefin, such as 1-hexene. However, the term "copolymer" is also inclusive of, for example, the copolymerization of a mixture of ethylene, propylene, 1-hexene,

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and 1-octene.

As used herein, the term "polymerization" is inclusive of homopolymerizations, copolymerizations, terpolymerizations, etc., and includes all types of copolymerizations such as random, graft, 5 block, etc. In general, the polymers in the films used in accordance with the present invention, can be prepared in accordance with any suitable polymerization process, including slurry polymerization, gas phase polymerization, and high pressure polymerization processes.

Slurry polymerization processes generally use superatmospheric pressures and temperatures in the range of 40°-100°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which are added ethylene and comonomers, and often hydrogen along with catalyst. 10 The liquid employed in the polymerization medium can be an alkane, cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization, and relatively inert. 15 Preferably, hexane or toluene is employed.

Alternatively, gas-phase polymerization processes utilize superatmospheric pressure and temperature in the range of about 50°-120°C. Gas phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles, in a pressure vessel adapted to permit the separation of product particles from 20 unreacted gases. Ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at temperatures of 50°-120°C. Triethylaluminum may be added as needed as a scavenger of water, 25 oxygen, and other impurities. Polymer product can be withdrawn continuously or semicontinuously, at a rate such as to maintain a constant product inventory in the reactor. After polymerization 30 and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the

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polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal.

High pressure polymerization processes utilize a catalyst system comprising a cyclopentadienyl-transition metal compound and an alumoxane compound. It is important, in the high-pressure process, that the polymerization temperature be above about 120°C., but below the decomposition temperature of the polymer product. It is also important that the polymerization pressure be above about 500 bar (kg/cm<sup>2</sup>). In those situations wherein the molecular weight of the polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen or reactor temperature, may be used in the process of this invention.

A heterogeneous polymer is a polymerization reaction product having a relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., typical polymers prepared, for example, using conventional Ziegler-Natta catalysts. Although there are a few exceptions (such as Ziegler-Natta catalyzed TAFMER (TM) linear homogeneous ethylene/alpha-olefin copolymers produced by Mitsui Petrochemical Corporation), heterogeneous polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

In contrast to heterogeneous polymers, homogeneous polymers are polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers are useful in various layers of the patch bag of the present invention. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular

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weight distribution. Furthermore, homogeneous polymers are typically prepared using metallocene, or other single-site type catalysis, rather than using Ziegler Natta catalysts.

More particularly, homogeneous ethylene/alpha-olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution ( $M_w/M_n$ ), composition distribution breadth index (CDBI), and narrow melting point range and single melt point behavior. The molecular weight distribution ( $M_w/M_n$ ), also known as polydispersity, may be determined by gel permeation chromatography. The homogeneous ethylene/alpha-olefin copolymers useful in this invention generally has ( $M_w/M_n$ ) of less than 2.7; preferably from about 1.9 to 2.5; more preferably, from about 1.9 to 2.3. The composition distribution breadth index (CDBI) of such homogeneous ethylene/alpha-olefin copolymers will generally be greater than about 70 percent. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent (i.e., plus or minus 50%) of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%. The Composition Distribution Breadth Index (CDBI) is determined via the technique of Temperature Rising Elution Fractionation (TREF). CDBI determination clearly distinguishes the homogeneous copolymers used in the present invention (narrow composition distribution as assessed by CDBI values generally above 70%) from VLDPEs available commercially which generally have a broad composition distribution as assessed by CDBI values generally less than 55%. The CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, in Wild et. al., J. Poly. Sci. Poly. Phys. Ed., Vol. 20, p.441 (1982). Preferably, the homogeneous ethylene/alpha-olefin copolymers have a CDBI greater than about 70%, i.e., a CDBI of from about 70% to 99%. In general, the

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homogeneous ethylene/alpha-olefin copolymers in the multilayer films of the present invention also exhibit a relatively narrow melting point range, in comparison with "heterogeneous copolymers", i.e., polymers having a CDBI of less than 55%. Preferably, the 5 homogeneous ethylene/alpha-olefin copolymers exhibit an essentially singular melting point characteristic, with a peak melting point ( $T_m$ ), as determined by Differential Scanning Calorimetry (DSC), of from about 60°C to 110°C. Preferably the homogeneous copolymer has a DSC peak  $T_m$  of from about 80°C to 100°C. As used herein, the 10 phrase "essentially single melting point" means that at least about 80%, by weight, of the material corresponds to a single  $T_m$  peak at a temperature within the range of from about 60°C to 110°C, and essentially no substantial fraction of the material has a peak melting point in excess of about 115°C., as determined by DSC 15 analysis. DSC measurements are made on a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data, i.e., the sample is heated at a programmed rate of 10°C./min. to a temperature below its critical range. The sample is then reheated (2nd melting) at a programmed rate of 10°C/min. 20 The presence of higher melting peaks is detrimental to film properties such as haze, and compromises the chances for meaningful reduction in the seal initiation temperature of the final film.

A homogeneous ethylene/alpha-olefin copolymer can, in general, be prepared by the copolymerization of ethylene and any one or more 25 alpha-olefin. Preferably, the alpha-olefin is a  $C_3$ - $C_{20}$  alpha-monoolefin, more preferably, a  $C_6$ - $C_{12}$  alpha-monoolefin, still more preferably, a  $C_4$ - $C_8$  alpha-monoolefin. Still more preferably, the alpha-olefin comprises at least one member selected from the group 30 consisting of butene-1, hexene-1, and octene-1, i.e., 1-butene, 1-hexene, and 1-octene, respectively. Most preferably, the alpha-olefin comprises octene-1, and/or a blend of hexene-1 and butene-1.

Processes for preparing and using homogeneous polymers are disclosed in U.S. Patent No. 5,206,075, U.S. Patent No. 5,241,031,

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and PCT International Application WO 93/03093, each of which is hereby incorporated by reference thereto, in its entirety. Further details regarding the production and use of homogeneous ethylene/alpha-olefin copolymers are disclosed in PCT International Publication Number WO 90/03414, and PCT International Publication Number WO 93/03093, both of which designate Exxon Chemical Patents, Inc. as the Applicant, and both of which are hereby incorporated by reference thereto, in their respective entireties.

Still another genus of homogeneous ethylene/alpha-olefin copolymers is disclosed in U.S. Patent No. 5,272,236, to LAI, et al., and U.S. Patent No. 5,278,272, to LAI, et. al., both of which are hereby incorporated by reference thereto, in their respective entireties.

The term "polyolefin" refers to any polymerized olefin, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted. More specifically, included in the term polyolefin are homopolymers of olefin, copolymers of olefin, copolymers of an olefin and an non-olefinic comonomer copolymerizable with the olefin, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include polyethylene homopolymer, polypropylene homopolymer, polybutene, ethylene/alpha-olefin copolymer, propylene/alpha-olefin copolymer, butene/alpha-olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, ethylene/butyl acrylate copolymer, ethylene/methyl acrylate copolymer, ethylene/acrylic acid copolymer, ethylene/methacrylic acid copolymer, modified polyolefin resin, ionomer resin, polymethylpentene, etc. Modified polyolefin resin is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., acrylic acid, methacrylic acid, isobutyl acrylate, or the like, or a derivative thereof such as the anhydride, ester, metal salt, or the like. It could also be obtained by incorporating into the olefin homopolymer

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or copolymer, an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like.

As used herein, terms identifying polymers, such as "ethylene/alpha-olefin copolymer", "polyamide", "polyester", "polyurethane", etc. are inclusive of not only polymers comprising repeating units derived from monomers known to polymerize to form a polymer of the named type, but are also inclusive of comonomers, derivatives, etc. which can copolymerize with monomers known to polymerize to produce the named polymer. For example, the term "polyamide" encompasses both polymers comprising repeating units derived from monomers, such as caprolactam, which polymerize to form a polyamide, as well as copolymers derived from the copolymerization of caprolactam with a comonomer which when polymerized alone does not result in the formation of a polyamide. Furthermore, terms identifying polymers are also inclusive of mixtures, blends, etc. of such polymers with other polymers of a different type.

Modified polymers, such as "modified ethylene/vinyl acetate copolymer", and "modified polyolefin" include such polymers having an anhydride functionality grafted thereon and/or copolymerized therewith and/or blended therewith. Preferably, such modified polymers have the anhydride functionality grafted on or polymerized therewith, as opposed to merely blended therewith.

The homogeneous ethylene/alpha-olefin copolymers useful in the bag film and patch film of the patch bag of the present invention include, for example, metallocene catalyzed polymers such as EXACT (TM) linear homogeneous ethylene/alpha-olefin copolymers obtainable from the Exxon Chemical Company, and TAFMER (TM) linear homogeneous ethylene/alpha-olefin resin obtainable from the Mitsui Petrochemical Corporation. All these homogeneous copolymers generally include copolymers of ethylene with one or more comonomers selected from C<sub>4</sub> to C<sub>10</sub> alpha-olefin such as butene-1

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(i.e., 1-butene), hexene-1, octene-1, etc. in which the molecules of the copolymers comprise long chains with relatively few side chain branches or cross-linked structures. This molecular structure is to be contrasted with conventional low or medium density polyethylenes which are more highly branched than their respective counterparts. For example, LLDPE has a density usually in the range of from about 0.91 grams per cubic centimeter to about 0.94 grams per cubic centimeter.

Another group of homogeneous ethylene/alpha-olefin copolymers are available from The Dow Chemical Company, and are known as AFFINITY (TM) long chain branched homogeneous ethylene/alpha-olefin copolymers. It has been discovered that AFFINITY (TM) long chain branched homogeneous ethylene/alpha-olefin copolymers are easier to process into films, relative to other homogeneous ethylene/alpha-olefin copolymers, such as EXACT (TM) linear homogeneous ethylene/alpha-olefin copolymers obtained from the Exxon Chemical Company. For this reason, among others, AFFINITY (TM) long chain branched homogeneous ethylene/alpha-olefin copolymers are preferred over EXACT (TM) linear homogeneous ethylene/alpha-olefin copolymers. Preferred long chain branched homogeneous ethylene/alpha-olefin copolymers have are those having a density of from about 0.87 to 0.94 g/cc, more preferably 0.89 to 0.92 g/cc. Long chain branched homogeneous ethylene/alpha-olefin copolymers are preferably produced using a metallocene-catalyzed polymerization reaction.

Although in the patch bag of the present invention the patch comprises homogeneous ethylene/alpha-olefin copolymer, the patch and/or the bag may further comprise heterogeneous ethylene/alpha-olefin copolymer. Several preferred heterogeneous ethylene/alpha-olefin copolymer include: linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), and ultra low density polyethylene (ULDPE).

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In general, both homogeneous and heterogeneous ethylene/alpha-olefin copolymers result from the copolymerization of from about 5 to 99 weight percent ethylene and from 1 to 20 weight percent alpha-olefin; preferably, from the copolymerization of from about 85 to 95 weight percent ethylene with 5 to 15 weight percent alpha-olefin.

As used herein, the phrases "inner layer" and "internal layer" refer to any layer, of a multilayer film, having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "outer layer" refers to any film layer of film having less than two its principal surfaces directly adhered to another layer of the film. The phrase is inclusive of monolayer and multilayer films. In multilayer films, there are two outer layers, each of which has a principal surface adhered to only one other layer of the multilayer film. In monolayer films, there is only one layer, which, of course, is an outer layer in that neither of its two principal surfaces are adhered to another layer of the film.

As used herein, the phrase "inside layer" refers to the outer layer, of a multilayer film packaging a product, which is closest to the product, relative to the other layers of the multilayer film.

As used herein, the phrase "outside layer" refers to the outer layer, of a multilayer film packaging a product, which is furthest from the product relative to the other layers of the multilayer film.

As used herein, the term "adhered" is inclusive of films which are directly adhered to one another using a heat seal or other means, as well as films which are adhered to one another using an adhesive which is between the two films.

As used herein, the phrase "directly adhered", as applied to film layers, is defined as adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other

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layer therebetween. In contrast, as used herein, the word "between", as applied to a film layer expressed as being between two other specified layers, includes both direct adherence of the subject layer between to the two other layers it is between, as well as including a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

Extrusion is the process of forming continuous shapes by forcing a molten plastic material through a die, followed by cooling or chemical hardening. Immediately prior to extrusion through the die, the relatively high-viscosity polymeric material is fed into a rotating screw of variable pitch, i.e., an extruder, which forces the polymeric material through the die.

Coextrusion is the process of extruding two or more materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure before chilling, i.e., quenching. Coextrusion can be employed in film blowing, free film extrusion, and extrusion coating processes.

The "machine direction" of a film is a direction along the length of the film, i.e., the direction in which the film is formed during extrusion and coating. In contrast, the "transverse direction" of a film is a direction across the film, perpendicular to the machine or longitudinal direction.

As used herein, the phrase "free shrink" refers to the percent dimensional change in a 10 cm x 10 cm specimen of film, when subjected to selected heat, as measured by ASTM D 2732, as known to those of skill in the art. ASTM D 2732 is described in the 1990 Annual Book of ASTM Standards, Section 8, Plastics, Vol. 08.02, pp. 368-371, which is hereby incorporated by reference thereto, in its entirety.

Although the films used in the patch bag according to the present invention can be monolayer films or multilayer films, the

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patch bag comprises at least two films laminated together. Preferably, the patch bag is comprised of films which together comprise a total of from 2 to 20 layers; more preferably, from 2 to 12 layers; and still more preferably, from 4 to 9 layers.

5 In general, the monolayer or multilayer films used in the patch bag of the present invention can have any total thickness desired, so long as the films provide the desired properties for the particular packaging operation in which the film is used, e.g. abuse-resistance (especially puncture-resistance), modulus, seal strength, optics, etc. However, for efficiency and conservation of resources, it is desirable to obtain the necessary puncture-resistance using the minimum patch thickness. Preferably, the film stock from which the patches are cut has a total thickness of from about 2 to 8 mils; more preferably, from about 3 to 6 mils.  
10 Furthermore, the patch film can be a monolayer film or a multilayer film. Several patch films described in detail below contain a total of 4, 6, and 14 layers.

15

Figure 1 is a side-view illustration of a preferred end-seal patch bag 20, in a lay-flat position, this patch bag being in accord with the present invention; Figure 2 is a cross-sectional view of patch bag 20 taken through section 2-2 of Figure 1.

20 Viewing Figures 1 and 2 together, patch bag 20 comprises bag 22, front patch 24 (i.e., first patch 24), and rear patch 26 (i.e., second patch 26), open top 28, and end-seal 30. The designations of "front" and "back"/"rear" are merely with respect to that side of patch bag 20 which is up when patch bag 20 is in its lay-flat position.

25 Figure 3A illustrates a cross-sectional view of preferred 3-layer film 36 for use as the stock material from which patches 24 and 26 can be cut. First layer 38 serves as an outside and puncture-resistant layer; second layer 40 serves as a tie layer and is preferably made up of two identical layers bonded to one

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another; third layer 42 serves as an inside layer and a puncture-resistant layer.

Figure 3B illustrates an enlarged cross-sectional view of the film of Figure 3A, including second layer 40 illustrated as being composed of identical film inner layers 44 and 46 adhering to one another. Inner layers 44 and 46 are preferably formed by collapsing a multilayer film tube having an inside layer which can be adhered to itself, resulting in what can be considered to be either a single central film layer, or a pair of identical film layers which are adhering to one another. Hence Figure 3A illustrates patch film 36 as a three layer film, whereas Figure 3B illustrates the same film as a four layer film, with the two inner layers being adhered to one another as represented by dotted line 48 because layers 44 and 46 can be considered to form a single layer since they are identical in thickness and chemical composition, due to the process used to make the film. The process illustrated in Figure 4, described in detail below, can be used to produce the film of Figure 3B.

Figure 3C illustrates a cross-sectional view of an alternative multilayer film 200 which can be used as stock material for preparing a patch for the patch bag of the present invention. Multilayer film 200 is a 7-layer film, and is described in detail in Patch Film No. 19, below. Multilayer film 200 is composed of outer layer 202, bulk layer 204, tie layer 206, O<sub>2</sub>-barrier layer 208, tie layer 210, bulk layer 212, and outer layer 214.

Figure 4 illustrates a schematic of a preferred process for producing the multilayer films of Figures 3A, 3B, and 3C. In the process illustrated in Figure 4, solid polymer beads (not illustrated) are fed to a plurality of extruders 52 (for simplicity, only one extruder is illustrated). Inside extruders 52, the polymer beads are forwarded, melted, and degassed, following which the resulting bubble-free melt is forwarded into die head 54, and extruded through annular die, resulting in tubing

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56 which is 5-40 mils thick, more preferably 20-30 mils thick, still more preferably, about 25 mils thick.

5 After cooling or quenching by water spray from cooling ring 58, tubing 56 is collapsed by pinch rolls 60, and is thereafter fed through irradiation vault 62 surrounded by shielding 64, where 10 tubing 56 is irradiated with high energy electrons (i.e., ionizing radiation) from iron core transformer accelerator 66. Tubing 56 is guided through irradiation vault 62 on rolls 68. Preferably, the irradiation of tubing 56 is at a level of from about 2 to 10 megarads (hereinafter "MR").

15 After irradiation, irradiated tubing 70 is directed over guide roll 72, after which irradiated tubing 70 passes into hot water bath tank 74 containing water 76. The now collapsed irradiated tubing 70 is submersed in the hot water for a retention time of at least about 5 seconds, i.e., for a time period in order to bring the film up to the desired temperature, following which supplemental heating means (not illustrated) including a plurality of steam rolls around which irradiated tubing 70 is partially wound, and optional hot air blowers, elevate the temperature of 20 irradiated tubing 70 to a desired orientation temperature of from about 240°F-250°F. Thereafter, irradiated film 70 is directed through nip rolls 78, and bubble 80 is blown, thereby transversely stretching irradiated tubing 70. Furthermore, while being blown, i.e., transversely stretched, irradiated film 70 is drawn (i.e., in 25 the longitudinal direction) between nip rolls 78 and nip rolls 86, as nip rolls 86 have a higher surface speed than the surface speed of nip rolls 78. As a result of the transverse stretching and longitudinal drawing, irradiated, biaxially-oriented, blown tubing film 82 is produced, this blown tubing preferably having been both 30 stretched at a ratio of from about 1:1.5 - 1:6, and drawn at a ratio of from about 1:1.5-1:6. More preferably, the stretching and drawing are each performed at a ratio of from about 1:2 - 1:4. The

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result is a biaxial orientation of from about 1:2.25 - 1:36, more preferably, 1:4 - 1:16.

5 While bubble 80 is maintained between pinch rolls 78 and 86, blown tubing 82 is collapsed by rolls 84, and thereafter conveyed through pinch rolls 86 and across guide roll 88, and then rolled onto wind-up roller 90. Idler roll 92 assures a good wind-up.

The invention is illustrated by the following examples, i.e., patch films, which are provided for the purpose of representation, and are not to be construed as limiting the scope of the invention. 10 Unless stated otherwise, all percentages, parts, etc. are by weight.

Patch Film Nos. 1, 2, 4, and 6-14, 16-17, and 19 are patch films which can be used to make a patch for a patch bag according to the present invention. Patch Film Nos. 3, 5, 15, and 18 are 15 comparative patch films to be contrasted to patch films which can be used to make the patch bag of the present invention.

#### Patch Film No. 1

A coextruded, two-ply tubular tape was cast, the tape having 20 a thickness of 29 mils, the tape having an A layer making up 85 percent of the tape thickness, and a B layer making up 15 percent of the tape thickness. The A Layer was composed of: (a) 87 weight percent DOWLEX 2045 (TM) linear low density polyethylene having a density of 0.920 g/cc, obtained from The Dow Chemical Company, of 25 Midland, Michigan (hereinafter "LLDPE #1"), (b) 10 weight percent ELVAX 3128 (TM) ethylene/vinyl acetate copolymer having a vinyl acetate content of 10 percent, obtained from DuPont, of Wilmington, Delaware, hereinafter "EVA #1", and (c) 3 weight percent TEKNOR EPE-9621C (TM) antiblock agent, obtained from Teknor Apex Plastics 30 Division, of Pawtucket, R.I., hereinafter "Antiblock #1". The B Layer contained 100 weight percent EXACT SLP 4008 linear homogeneous ethylene/alpha-olefin plastomer having a density of

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0.885 g/cc, obtained from the Exxon Chemical Company, of Baytown, Texas (hereinafter, "linear homogeneous ethylene/alpha olefin #1").

The two-ply tubing was cooled to a solid phase in a water bath and then electronically crosslinked with a 500 Kev beam to a level of from about 2 to 10 MR. The resulting crosslinked two-ply tubing was heated by steam cans and hot air at about 210-220°F, and was subsequently oriented by being drawn and stretched approximately 350%, in each of the machine and transverse directions, respectively, using a trapped bubble of air held between two nip rolls. The orientation produced a 2.25 mil two-ply film in the form of a tube.

After drawing, the resulting tube of hot-water-shrinkable flat film was passed through a pair of nip rolls, causing the inside B layer to bond to itself upon tube collapse, rendering a final four-ply film, with the "middle" plies being the inside B layer bonded to itself (i.e., resulting in a "4-ply" film having a thickness of 4.5 mils), as follows:

20

	A	B	B	A	
25	Blend A	SLP 4008	SLP 4008	Blend A	

30

Table I, immediately below, includes the chemical composition and thickness of each of the layers, together with the function which the layer serves in the patch.

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TABLE I

Fig. 3 layer desig- nation	layer function	chemical identity	layer thickness (mils)
5	38 outside layer & puncture-resistant layer	87% LLDPE #1; 10% EVA #1; 3% Antiblock #1	2.0
10	40 tie layer	homogeneous ethylene/ alpha-olefin #1	0.7
15	42 inside layer & puncture-resistant layer	87% LLDPE #1; 10% EVA #1; 3% Antiblock #1	2.0

20

Patch Film No. 1 was composed of the above three layers, the middle layer being composed of the inside tube layer adhered to itself. Patch Film No. 1 was determined to have a free shrink at 185°F (via ASTM 2732), and an instrumented impact, as set forth below in Table II, below. Instrumented impact was measured by a procedure substantially equivalent to ASTM D 3763. ASTM D 3763 is described in the 1990 Annual Book of ASTM Standards, Section 8, Plastics, Vol. 08.03, pp. 174-178, which is hereby incorporated by reference thereto, in its entirety.

30 An alternative to Patch Film No. 1 is a two-layer film having a thickness of about 4.5 mils, with about 85 weight percent of this film having a composition corresponding to layer 38 described in Table I above, and with 15 weight percent of this film having a composition corresponding to layer 40 above. This film could be produced using a flat die, rather than a circular die.

#### Patch Film No. 2

35 Patch Film No. 2 was prepared by the same process employed to produce Patch Film No. 1, with the exception that in Patch Film No.

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2, the A Layer was composed of a blend of: (a) 87 weight percent LLDPE #1, (b) 10 weight percent EXACT 3032 (TM) linear homogeneous ethylene/alpha-olefin plastomer having a density of 0.900 g/cc, also obtained from the Exxon Chemical Company (hereinafter, "linear homogenous ethylene/alpha-olefin copolymer #2), and (c) 3 weight percent Antiblock #1. In Patch Film No. 2, the B Layer remained identical to the B Layer of Patch Film No. 1. Furthermore, as with Patch Film No. 1, in Patch Film No. 2 the A Layer made up 85 percent of the tape thickness, and a B layer made up 15 percent of the tape thickness. The Patch Film No. 2 free shrink and instrumented impact are provided in Table II, below.

Patch Film No. 3 (Comparative)

Patch Film No. 3 was prepared by the same process employed to produce Patch Film No. 1, except that in Patch Film No. 3, the A Layer was composed of a blend of: (a) 87 weight percent LLDPE #1, (b) 10 weight percent ELVAX 3128 (TM) ethylene/vinyl acetate copolymer having a vinyl acetate content of 9 percent and a density of 0.928 g/cc, and a melt index of 2.0, obtained from the DuPont Chemical Co., of Wilmington, Delaware (hereinafter referred to as EVA #2), and (c) 3 weight percent Antiblock #1. In Patch Film No. 3, the B Layer was composed of 100 weight percent ELVAX 3175 (TM) ethylene/vinyl acetate copolymer having a vinyl acetate content of 28 percent and a density of 0.950 g/cc, and a melt index of 6.0, obtained from the DuPont Chemical Co., of Wilmington, Delaware (hereinafter referred to as EVA #2). Furthermore, as with Patch Film No. 1, in Patch Film No. 3 the A Layer made up 85 percent of the tape thickness, and a B layer made up 15 percent of the tape thickness.

The Patch Film No. 3 free shrink and instrumented impact are provided in Table II, below. Patch Film No. 3 is a comparative patch film because it does not comprise any homogeneous ethylene/alpha-olefin copolymer.

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#### Patch Film No. 4 (Comparative)

Patch Film No. 4 was prepared by the same process employed to produce Patch Film No. 1, except that in Patch Film No. 4, the A Layer was composed of a blend of: (a) 82 weight percent LLDPE #1, (b) 15 weight percent EVA #1, and (c) 3 weight percent Antiblock #1. In Patch Film No. 4, the B Layer was composed of 100 weight percent EVA #2. Furthermore, as with Patch Film No. 1, in Patch Film No. 4 the A Layer made up 85 percent of the tape thickness, and a B layer made up 15 percent of the tape thickness.

The Patch Film No. 4 free shrink and instrumented impact are provided in Table II, below. Patch Film No. 4 is a comparative patch film because it does not comprise any homogeneous ethylene/alpha-olefin copolymer.

#### Patch Film No. 5

Patch Film No. 5 was prepared by the same process employed to produce Patch Film No. 1, except that in Patch Film No. 5, the A Layer was composed of a blend of: (a) 67 weight percent LLDPE #1; (b) 30 weight percent XU59220.01, a proprietary experimental long chain branched homogeneous ethylene/alpha-olefin copolymer (hereinafter referred to as "homogeneous ethylene/alpha-olefin #3") having a density of 0.901 g/cc and a melt index of 0.9, obtained under a development agreement with The Dow Chemical Company of Midland, Michigan; and, (c) 3 weight percent Antiblock #1. The information concerning XU59220.01 and the evaluation results of film/bag containing the experimental polymer which are set forth in this example have been approved for release by Dow.

In Patch Film No. 5, the B Layer was composed of 100 weight percent EVA #2. Furthermore, as with Patch Film No. 1, in Patch Film No. 5 the A Layer made up 85 percent of the tape thickness, and a B layer made up 15 percent of the tape thickness.

The Patch Film No. 5 free shrink and instrumented impact are provided in Table II, below.

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TABLE II

	Film No.	Free Shrink at 185°F %MD , %TD	Free Shrink at 205°F %MD , %TD	Impact Strength (lbs)	Energy to Break (ft-lbs)
5	1	11 16	20 30	97	4.8
10	2	11 18	21 32	109	5.7
	3 (comparative)	10 17	20 30	100	5.0
15	4 (comparative)	13 18	25 32	87	3.1
	5	14 20	-- --	88	3.2

As can be seen from Table II, the impact strength of various patch films according to the present invention, e.g., Patch Film Nos. 1, 2, and 5, were found to be comparable to the impact strength exhibited by comparative Patch Film No. 3 and comparative Patch Film No. 4, both of which utilize LLDPE as the polymer which provides the patch film with high impact strength. Thus, it has been found that the use of homogeneous ethylene/alpha-olefin copolymers, in accordance with the present invention, can result in a patch film having an impact strength substantially equivalent to, and in some instances even better than, the impact strength of LLDPE-based patch films.

## Patch Film No. 6

A coextruded, two-ply, tubular tape was cast; the tape having a thickness of 9 mils, the tape having an A layer making up 85 percent of the tape thickness, and a B layer making up 15 percent of the tape thickness. The A Layer was composed of a blend of: (a) 50 weight percent of a resin composition referred to as ECD 103 linear homogeneous ethylene/hexene copolymer, also obtained from the Exxon Chemical Company (hereinafter referred to as "linear homogeneous ethylene/alpha-olefin #4"), (b) 37 weight percent ECD

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106 linear homogeneous ethylene/hexene copolymer, having a density of about 0.917g/cc, and a melt index of about 3, also obtained from the Exxon Chemical Co. (hereinafter referred to as "linear homogeneous ethylene/alpha-olefin #5"), (c) 10 weight percent LD 5 200.48 (TM) low density polyethylene having a density of 0.917 g/cc and a melt index of 6.7, this low density polyethylene also obtained from the Exxon Chemical Co., and (d) 3 weight percent Antiblock #1. In Patch Film No. 6, the B Layer was composed of 100 weight percent EVA #2.

10 The two-ply sheet was cooled to a solid phase using a chilled roll, and then electronically crosslinked with a 500 Kev beam to a level of approximately 2 to 10 MR. The resulting crosslinked two-ply sheet was heated with hot air (at 210-220°F), and was subsequently oriented by drawing and stretching approximately 300 15 percent in each of the machine and transverse directions, respectively, using a tenter frame, to produce a biaxially oriented film having a thickness of about 1 mil. The impact strength of the resulting Film No. 6 is provided in Table III, below.

20 Patch Film No. 7

A coextruded, two-ply sheet is cast, the sheet having a thickness of 18 mils, the sheet having an A layer making up 85 percent of the sheet thickness, and a B layer making up 15 percent of the sheet thickness. The A Layer is composed of: (a) 25 97 weight percent linear homogeneous ethylene/alpha-olefin #4, and (b) 3 weight percent Antiblock #1. In Patch Film No. 7, the B Layer is composed of 100 weight percent EVA #2.

The two-ply sheet is cooled to a solid phase using a chilled roll, and then electronically crosslinked with a 500 Kev beam to a level of approximately 2 to 10 MR. The resulting crosslinked two-ply sheet is heated with hot air (at 210-220°F), and is subsequently oriented by drawing and stretching approximately 300 percent in each of the machine and transverse directions,

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respectively, using a tenter frame, to produce a biaxially-oriented film having a thickness of about 2 mils.

Patch Film No. 8

5 A single ply sheet is cast, the sheet having a thickness of 18 mils, the sheet being composed of a blend of: (a) 97 weight percent linear homogeneous ethylene/alpha-olefin #4, and (b) 3 weight percent Antiblock #1. After the sheet is cast, the tape is cooled to a solid phase using a chilled roll, and then 10 electronically crosslinked with a 500 Kev beam to a level of approximately 2 to 10 MR. The resulting crosslinked two-ply sheet is heated with hot air (at 210-220°F), and is subsequently oriented, using a tenter frame, to impart longitudinal orientation in an amount of about 300 percent, and transverse orientation in an 15 amount of about 300 percent, to result in a biaxially oriented film having a thickness of about 2 mils.

Patch Film No. 9

20 A single ply tubular tape is cast, the tape having a thickness of 27 mils, the tape being composed of a blend of: (a) 97 weight percent linear homogeneous ethylene/alpha-olefin #4, and (b) 3 weight percent Antiblock #1. After the tape is cast, the tape is cooled to a solid phase using chilled air or chilled water, and then 25 electronically crosslinked with a 500 Kev beam to a level of approximately 2 to 10 MR. The resulting crosslinked tape is then heated with hot air (at 210-220°F), and is subsequently oriented by drawing and stretching approximately 300 percent in each of the machine and transverse directions, respectively, using a trapped bubble process, to produce a biaxially-oriented film having a 30 thickness of about 3 mils. The tubular film is thereafter slit to form a flat film suitable for use as a patch on a patch bag.